

# Quantum Dot Solar Cells: High Efficiency through Multiple Exciton Generation

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## ABSTRACT

Impact ionization is a process in which absorbed photons in semiconductors that are at least twice the bandgap can produce multiple electron-hole pairs. For single-bandgap photovoltaic devices, this effect produces greatly enhanced theoretical thermodynamic conversion efficiencies that range from 45 - 85%, depending upon solar concentration, the cell temperature, and the number of electron-hole pairs produced per photon. For quantum dots (QDs), electron-hole pairs exist as excitons. We have observed astoundingly efficient multiple exciton generation (MEG) in QDs of PbSe (bulk  $E_g = 0.28$  eV), ranging in diameter from 3.9 to 5.7 nm ( $E_g = 0.73, 0.82,$  and  $0.91$  eV, respectively). The effective masses of electron and holes are about equal in PbSe, and the onset for efficient MEG occurs at about three times the QD HOMO-LUMO transition (its “bandgap”). The quantum yield rises quickly after the onset and reaches 300% at  $4 \times E_g$  (3.64 eV) for the smallest QD; this means that every QD in the sample produces three electron-hole pairs/photon.

### 1. Objectives

This work addresses MEG and carrier energy relaxation processes in semiconductor QDs. Our aim is to determine how the efficiency of MEG is influenced by the change in physical properties related to quantum confinement in semiconductor nanoparticles. The ultimate objective is to use a QD semiconductor system with highly efficient MEG to fabricate a high-efficiency solar cell.

### 2. Technical Approach

We are studying MEG quantum yields and energy relaxation rates in QDs using fs pump-probe transient absorption techniques [1].

### 3. Results and Accomplishments

To study MEG processes in QDs, we detect multiexcitons created via exciton multiplication (EM) by monitoring the signature of multiexciton decay in the transient absorption (TA) dynamics, while maintaining a pump photon fluence lower than that needed to create multiexcitons directly. The Auger recombination rate is proportional to the number of excitons per QD with the decay of a biexciton being faster than that of the single exciton. By monitoring the fast-decay component of the TA dynamics at low pump intensities we can measure the population of excitons created by MEG. The transients are detected with either a band-edge probe photon that monitors the band-edge bleach or a mid-IR photon that

probes intraband transitions in the newly created excitons.

We have measured the MEG quantum yield (QY) in colloidal PbSe QDs with diameters ranging from 3.9 to 5.7 nm, corresponding to QD bandgaps ranging from 0.91 to 0.73 eV. For all the PbSe QD samples the onset for efficient MEG occurs at about three times the energy gap, a result in agreement with that reported by Schaller and Klimov [2]. Our data show that QYs  $> 2$  can be achieved at higher photon energy, meaning that three electron/hole pairs per photon have been created by MEG.

For the 3.9 nm QD ( $E_g = 0.91$  eV), the QY reaches a surprising value of 3.0 at  $E_h/E_g = 4$ . This means that on average every QD in the sample produces three excitons/photon. The sharper rise of the QY in the smallest diameter sample compared to the other two larger samples may be due to the different surface passivation conditions. The 3.9 nm QD sample was treated with oleic acid and oleylamine to improve the surface passivation, which greatly increased the single-exciton lifetime. More work is warranted to understand what role the surface plays in efficient MEG.

For MEG to be the dominant cooling process, its rate must be much faster than the competing cooling rates of excited excitons by phonon emission. In PbSe QDs, the fast cooling by the Auger process is expected to be inhibited because of the large spacing between both hole and electron levels which is a consequence of the nearly equal electron and hole effective mass in PbSe. With Auger cooling inefficient, we may expect cooling rates of a few ps, as is observed in other QD systems where the phonon bottleneck is operative. A new and unique model to explain the details of MEG in QDs has been proposed [1]

In theoretical efficiency calculations [3] of solar cells with impact ionization (II) included as a charge generation process, a stair step QY, representing the energetic maximum QY that can be obtained from II, is used with an idealized detail balance model to calculate the maximum expected efficiency vs  $E_g$ . We have developed an alternate approach to incorporate idealized or experimentally determined II QYs into a numerical device simulator, which allows us to explore the potential benefits of II on cell performance. This approach also allows us to incorporate deviations from ideal behavior (Auger, trap and surface recombination, finite-carrier mobilities, incomplete absorption, etc.) into the device model. When II is active in a material, the total generation rate (optical plus II) can be written as:

$$G(x) = \Sigma(1 + QY_{II}) \exp(-x) \quad (1)$$

where  $\alpha$  is the absorption coefficient,  $\Phi_{\text{ph}}$  is the solar photon flux, and the summation covers the energies above the bandgap.

Through simulations, we have compared the performance of an idealized device having the different  $\text{QY}_{\text{II}}$  models shown in Fig. 1.

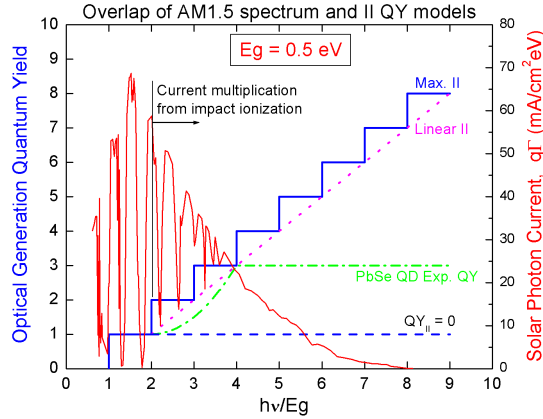


Fig. 1. QY models used in the device simulations.

We investigated four  $\text{II QY}$  models: the case of no  $\text{II}$ , the experimentally measured  $\text{QY}_{\text{II}}$  of PbSe QDs shifted to  $E_g$ , a linear  $\text{QY}_{\text{II}}$ , and the energetic maximum  $\text{QY}$  that can be obtained from  $\text{II}$ . Charge generation from  $\text{II}$  for absorbed photons above twice the bandgap will add to the usual optical generation from absorbed photons with  $h\nu > E_g$ .

To calculate theoretical efficiencies with the above  $\text{II}$  models, we used a simple, idealized pn-junction configuration with a total length of 3.7  $\mu\text{m}$ . The absorption coefficient was taken to have a square-root energy dependence rising to  $10^5 \text{ cm}^{-1}$  at  $h\nu = 4 E_g$ , which insured  $\sim 100\%$  absorption of photons with  $h\nu > E_g$ . Both radiative and Auger recombination mechanisms were included with a radiative B coefficient of  $10^{-10} \text{ cm}^6/\text{s}$  and an Auger coefficient of  $8 \times 10^{-28} \text{ cm}^3/\text{s}$ . The mobility of electrons and holes was taken to be  $100 \text{ cm}^2/\text{Vs}$  and the n- and p-side doping was  $10^{17} \text{ cm}^{-3}$ . In these initial calculations, we neglected minority carrier surface recombination and trap recombination. The cell efficiency vs.  $E_g$  over the range 0.5 to 1.5 eV is shown in Fig. 2.

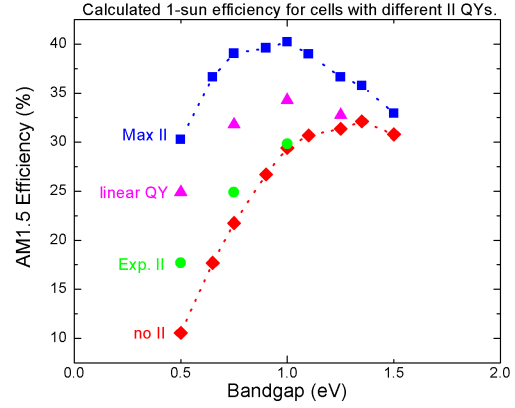


Fig. 2. Calculated efficiencies for different  $\text{QY}_{\text{II}}$  models.

Under unconcentrated AM1.5 illumination, a cell with maximal  $\text{II}$  has the potential to reach  $\sim 41\%$  efficiency at  $E_g \sim 1 \text{ eV}$ . The efficiencies calculated using the experimentally determined  $\text{II QY}$  of PbSe QDs are lower than the maximum values, because of the slow rise of the  $\text{QY}$  above  $2x E_g$ . The improvement over the “no  $\text{II}$ ” case is much better, however, for lower bandgaps. This implies that lower-gap QDs with a fast turn-on in  $\text{QY}_{\text{II}}$  will be required for significant efficiency enhancements in QD solar cells.

#### 4. Conclusions

We have observed very high  $\text{QY}$ s because of multiple exciton generation in PbSe QDs, reaching up to 300% at  $4x E_g$ . Future work will explore the dependence of QD size, electronic structure, and related semiconductor properties on MEG, and will also model the performance of QD-sensitized mesoporous solar cells that are based on impact ionization in QDs.

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